CHARACTERIZATION AND MONITORING OF DENSE NON-AQUEOUS PHASE LIQUIDS

TECHNOLOGY NEED

Residual industrial solvents, primarily dense non-aqueous phase liquids (DNAPLs), are currently the most significant challenge for the successful completion of many large groundwater and soil cleanup efforts. Slowly dissolving DNAPLs provide a major source of groundwater contamination for hundreds of years. Adding to the challenge is the fact that DNAPLs are very difficult to characterize in the subsurface--especially when they are found in dispersed blobs as is typical at many sites. At waste sites where DNAPLs are suspected, robust characterization of the nature and extent of the contamination must be a key component of any comprehensive remediation strategy. Traditional sampling approaches generally are not successful at locating DNAPLs and a focused strategy based on an appropriate conceptual model should be used. Above the water table, residual DNAPLs will reside in intergranular pores held by capillary forces. Below the water table, DNAPLs behave in a complex fashion, moving downward as an immiscible phase and accumulating in highly concentrated discrete and disbursed ganglia. Because of the physical and chemical characteristics of DNAPLs, characterization and remediation methods that minimize unnecessary waste generation are prudent. Finally, precise delineation of DNAPL areas will facilitate the design of appropriate remediation strategies and help keep cleanup costs from escalating.

TECHNOLOGY DESCRIPTION

The central thrust of the characterization task includes detecting DNAPLs consistently, minimizing the creation of preferred pathways for contaminant migration, emphasizing small-scale tests, and generating data to optimize cleanup activities. Because of these design concepts, the proposed technologies are required to target the thin, highly discrete DNAPL zones typical of most sites. The DNAPL characterization tools include:

- Hydrophobic sorbent pads on SEAMIST™ membrane.
- Laser-induced fluorescence (LIF), Raman, and Optical CPT probes.
- Small-scale partitioning gas tracer tests above the water table.
- Core Penetrometer Testing (CPT) alcohol micro injection/extraction.
- CPT enhanced spectral gamma probe.

These technologies, for example, surface geophysics and large-scale differential tracer tests, will complement tools currently used or proposed by industry, the U.S. Environmental Protection Agency (EPA), and the U.S. Department of Defense (DoD). The innovative characterization technologies, for example, CPT-based Raman and SEAMIST™, build on the baseline DNAPL characterization techniques and generally strive for direct detection of DNAPLs with minimal invasion and minimal investigation-derived waste (IDW). All of the DNAPL research and development projects at SRS are selected based on targets driven by site cleanup goals and local and regional regulatory requirements.

A coordinated package of innovative DNAPL characterization tools is being developed and deployed. Each technology is carefully designed to:

- Minimize secondary waste.
- Eliminate undesirable gravitational movement of DNAPLs.
- Minimize IDW.
- Mitigate similar types of collateral environmental damage inherent in addressing this complex environmental need.

Rapid Hydrophobic Sampling. Small diameter SEAMIST™ membranes with hydrophobic sorbent (preferentially absorbs non-polar liquids) pads fixed to the liner are designed to collect DNAPL samples. The system is fast and easy to deploy with a cone penetrometer system and yields depth-discrete samples from boreholes. The pads are pressed against the formation on the walls of the borehole and the hydrophobic material preferentially collects organic liquids. The liner is then retrieved from the borehole and rapidly scanned using a volatile organic compound (VOC) analyzer. After screening, the depth-discrete sorbent pads can be analyzed in more detail in the laboratory.

Laser Induced Fluorescence (LIF), Optical and Raman-Cone Penetrometer Methods. The cone penetrometer is particularly suited for characterization of DNAPL sites because of the relative ease to delineate depth-discrete lithology and contaminant distribution as well as the ability to deploy a variety of sensors. Although LIF sensors cannot directly measure chlorinated alkanes (because these compounds do not fluoresce at standard excitation wavelengths), fluorescent intensities are found to increase (1-3 orders of magnitude over the background) in zones known to contain DNAPLs. The large increase may be due to leaching of natural organic matter or the incorporation of other likely fluorophores into the DNAPLs. Co-disposed lubricants, hydraulic oils, and cutting oils are also potential candidates for fluorescence probing. Thus, the fluorescence measurements can be used to infer the presence of DNAPLs. Used in concert with Raman spectra, the presence of DNAPLs in a particular location can be confirmed.

Raman spectroscopy is one of the few direct detection characterization technologies for DNAPLs. Each compound has a unique Raman spectrum that can be probed through the optics deployed in a cone penetrometer. Thus, specific DNAPL compounds can be identified. Unfortunately, the Raman technique is inherently weak and the spectra must be separated from the often dominating fluorescence spectrum.

Other optical techniques such as CPT video microscopy will also help identify DNAPLs in the subsurface. Specific formations can be visually identified for DNAPL potential for precise targeting by spectroscopy. If co-constituents color the DNAPL, DNAPL may be directly identified.

Differential Partitioning Gas Tracer Tests. These tests can be used to determine the presence and the mass transfer behavior of DNAPLs held in fine-grained sediments in the vadose zone. Two or more hydrophobic tracer gases are injected in one vadose zone well and extracted from a nearby vadose zone well. The tests are designed such that one of the gases has a strong partitioning coefficient to hydrophobic organic liquid phases while the other gas is relatively inert with respect to both water and organics. The different arrival times of the two gases at the extraction well are measured and provide information on residual DNAPL phase in the probe zone between the two wells. The deployment of the differential partitioning tracer test in the vadose zone is difficult because most of the DNAPL above the water table at the Savannah River Site (SRS) testing area is trapped in clay layers. This is true for many sites across the country. Thus, in this case, the data can be used to evaluate whether or not DNAPL is present and to estimate the mass transfer into the sand zones. Since most of the airflow during soil cleanup is in the sand zones, the differential tracer tests are useful in estimating cleanup time.

Small-Scale Alcohol Micro Injection/Extraction Test. The single-well, alcohol injection-extraction test in this program uses a cone penetrometer delivery system and less than one gallon of injection volume. The injected fluid, a solution of alcohol that can solubilize DNAPL without mobilizing it, permeates into an area the size of a small cylinder around the CPT. A small volume of water is injected a small distance into the formation (< 1') and then extracted. Samples of the water are analyzed for concentrations of organic contaminants. Then, a small volume of an alcohol and water solution is injected a similar distance into the formation (< 1') and then extracted. The extracted solution is sampled and analyzed. DNAPL will be much more soluble in the alcohol/water solution than in water alone. A large increase in the concentration of DNAPL components is an unequivocal indicator of the presence of residual DNAPL. The test provides clear confirmation of DNAPL without having to drill additional holes. The test will be used to target a specific stratum that is likely to contain DNAPL (i.e., above clay in the saturated zone).

Spectral Gamma Probe. Natural radioactivity in the subsurface tends to fractionate in DNAPL preferentially over groundwater because of the high partition coefficient of radon into DNAPL. Task investigators first observed this phenomenon of elevated radon measurements during a solvent recycle test. The solvent recovered during the test was found to be radioactive. Below the water table, where DNAPLs occur in sands just above clay layers, the spectral gamma signal will indicate a clear doublet. The clay zone gamma signal will show the presence of primarily potassium (K) with uranium (U) and thorium (Th) parents in equilibrium with radon daughters. The overlying DNAPL zone will show less K, indicating decreased amounts of clay in the sand unit, with elevated U and Th series gamma signals strongly shifted to radon daughters. A similar scenario has been described for DNAPLs above the water table. The affinity of radon for DNAPLs is about 25 times greater than its affinity for water. By measuring the ratio of gamma-emitting radon parent- to radon-daughter concentrations with a spectral gamma probe, direct identification of zones of DNAPLs may be accomplished. The theoretical basis of the work was confirmed: hypothetical spectral gamma signatures for DNAPLs above and below the water table were generated. The spectral gamma logging technique provides detailed information about the location of DNAPLs without additional drilling and with minimal IDW. The emphasis for this project in FY 1998 is to publish a handbook on techniques for characterizing DNAPLs in the subsurface.

BENEFITS

Many of the current baseline methods used for characterizing a suspected DNAPL site are described in Cohen and Mercer (1993). These methods generally consist of inferred measurements of DNAPLs (e.g., soil-gas analysis, geophysical methods), rule-of-thumb empirically developed methods from well samples, and direct measurements using invasive methods such as drilling and soil sampling. Most geophysical techniques do not have the resolution needed to detect DNAPLs occurring at scales of far less than one cubic meter. Conventional soil and liquid sampling are too costly and produce significant quantities of IDW.

Several of the techniques described here were designed specifically for implementation with the cone penetrometer. This takes advantage of the high-resolution geologic information obtained with the Cone Penetrometer Truck (CPT) and minimizes the production of IDW.

Because of the complexity of DNAPLs in the subsurface, all DNAPL characterization methods should be used in an ensemble approach where DNAPLs in an area are postulated with a probability determined from the weight of evidence of the data from several characterization techniques.

CAPABILITIES/LIMITATIONS

By emphasizing safety and small-scale direct DNAPL detection, the technologies provide the most accurate possible information about the precise intervals where DNAPL occurs, leading to optimized remediation design. The technologies in this task reduce waste and improve the precision of delineating DNAPL zones. The CPT technologies are limited to unconsolidated sediments and to depth refusal of the CPT truck. The CPT investigations are limited to the sediments in contact with the probe. The differential partitioning gas tracer tests are limited to the vadose zone.

COLLABORATION/TECHNOLOGY TRANSFER

This work is a collaborative effort between various federal agencies, universities, and private industry. Principal partners include Clemson University, EIC Laboratories, FLUTE Limited, U.S. Army Corps of Engineers, NFESC, NCCOSC, U.S. Geological Survey (USGS), ARA, Fugro, Water Development Corporation, R J Electronics, Oak Ridge National Laboratory (ORNL), and Argonne National Laboratory (ANL). Additional collaboration has been obtained from Intera, University of Texas, EPA, the U.S. Air Force, and others.

ACCOMPLISHMENTS

- Inferred detection of DNAPLs using LIF at several waste sites.
- First *in situ* identification of PCE using Raman spectroscopy at SRS.
- Inferred detection of DNAPL using differential partitioning gas tracer tests and quantitative limitations of this technique.
- First deployment of SEAMIST™ membrane in a cone penetrometer hole.

TECHNICAL TASK PLAN (TTP) INFORMATION

TTP No./Title: SR17C221 - Development and Deployment of Innovative DNAPL Characterization Methods. Related TTP No./Title.-.SR18SS32 - Applied DNAPL Characterization Methods

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This specially equipped truck can go from location to location and characterize and monitor Dense Non-Aqueous Phase Liquids (DNAPL) in the subsurface.